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Density-functional calculations of the electronic structures and magnetism of the pnictide superconductors $BaFeAs_2$ and $BaFeSb_2$

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We investigate the structural, electronic, and magnetic properties of the hypothetical compound $BaFePn_2$ (Pn=As and Sb), which is isostructural to the parent compound of the high-temperature superconductor $LaFeAsO_{1-x}F_x$. Using density-functional theory, we show that the Fermi surface, electronic structure, and spin-density wave instability of $BaFePn_2$ are very similar to the Fe-based superconductors. Additionally, there are very dispersive metallic bands of a spacer Pn layer, which are almost decoupled from FePn layer. Our results show that experimental study of $BaFePn_2$ can test the role of charge and polarization fluctuation as well as the importance of two dimensionality in the mechanism of superconductivity.

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The discovery of superconductivity in iron oxypnictide $LaFeAsO_{1-x}F_x$ (Ref. 1) has generated renewed interest in the phenomena of high-temperature superconductivity and brought the transition-metal-based compounds to the forefront of condensed-matter research. The basic units responsible for the superconductivity are the fluorite-type $[Fe_2Pn_2]$ layers, with Pn as a pnictide element (P, As, Sb, and Bi). These layers are separated by spacer layers, which play the role of charge reservoir. The first class of materials studied has the ZrCuSiAs structure (1111 compounds), where the spacer layer $[Ln_2O_2]$ has the "antifluoride" or Pb_2O_2 structure. With Ln=Sm, critical temperature higher than 55 K has been achieved.[2] Superconductivity with $T_c=38$ K was also found in the ternary compounds AFe_2As_2,[3] with A=Ca, Sr, or Ba, (122 compounds) with $ThCr_2Si_2$ structure. Superconductivity with $T_c=18$ K was also achieved in LiFeAs.[4] The crystal structure of this compound is of the PbFCl type and consists of parallel Fe_2As_2 layers separated by a Li double layer spacer. Iron-based superconductivity has also been realized in binary iron chalcogenides. In the α-$FeSe_{1-x}$ compound under pressure, transition temperature can reach 27 K.[5] In this compound the need for charge reservoir spacer layer is eliminated and deviation from the Fe d^6 configuration is obtained by Se vacancies. The iron layers are very similar to the ones found in the iron pnictide materials.

Band-structure calculations for these compounds revealed fairly quasi-two-dimensional bands near the Fermi level with a large d character and a characteristic Fermi surface featuring two electron pockets around the M point and two hole pockets around the Γ point in the Brillouin zone.[6] In all these examples, the spacer layer is insulating (or absent in the binary iron chalcogenides). The bands derived from the spacer layers are far from the Fermi level. Thus the role of the spacer layer is to provide a charge reservoir which keeps the charge of the FeAs unit near −1. In an ionic picture, this corresponds to As^{3-} and Fe^{2+}, i.e., the Fe atoms are in a d^6 configuration.

There is no concensus yet on the mechanism of superconductivity in this system. Our early calculation,[7] as well as the more extensive studies in Refs. 8 and 9, rule out a phonon mechanism. However, both spin and orbital fluctuations,[9–11] as well as the polarizability of the As,[12,13] have been suggested as potential candidates for the pairing glue. Understanding the mechanism of superconductivity and the factors controlling the critical temperature is of great fundamental interest, as well as of practical importance. Hence, numerous related compounds are being explored theoretically and experimentally.

In this Rapid Communication, we identify two hypothetical compounds (112 compounds) in the iron pnictide class: $BaFeAs_2$ and $BaFeSb_2$ with the $ZrCuSi_2$ type. They are isostructural with LaFeAsO, as shown in Fig. 1. Although they have not yet been synthesized, their isostructural compounds, $LnMAs_2$ and $LnMSb_2$, have been studied intensively with various kinds of rare earth Ln and transition metals M.[14–16] So, one can expect that $BaFeSb_2$ as well as $BaFeAs_2$ can be synthesized. We will show here, using density-functional theory (DFT) calculation, that the fermiology derived from FeAs layers is very similar to those of previously studied iron pnictides. There is, however, a very important difference between all known Fe superconductors and these two compounds. Namely, the spacer layer BaPn is *metallic*.

This is of interest because it allows us to modify the interaction strength in the charge channel without altering significantly the one-body part of the Hamiltonian. The 112 family provides a microscopic realization of the idea of a sandwich structure, in which a good metallic layer is inserted between correlated superconductors. Its experimental investigation will shed further light on the importance of correlations in the iron pnictides compounds and on the role of charge and polarization fluctuations in the pairing.

In order to predict the structural, electronic, and magnetic structures of hypothetical compound $BaFe_2Pn_2$ (Pn =As,Sb), we used the full-potential linearized augmented plane-wave method as implemented in WIEN2K code.[17] The generalized gradient approximation has been used for the exchange correlation function.[18] The 1000 k points are used for the full Brillouin-zone integration. Employed muffin-tin radii for Ba, Fe, As, and Sb are 2.5, 2.24, 1.98, and 2.09 a.u., respectively. The lattice parameters as well as internal positions have been optimized by the total-energy minimization assuming spin-density wave (SDW) ground state with tetragonal structure. We also check that different types of magnetic ordering give similar structural parameters. It was shown in

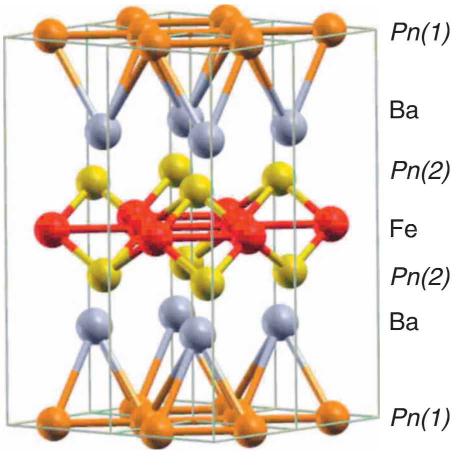

FIG. 1. (Color) Crystal structure of BaFePn_2 (Pn=As and Sb). Ba, Fe, $Pn(1)$, and $Pn(2)$ atoms are denoted by gray, red, orange, and yellow spheres, respectively. There are two type of Pn: $Pn(1)$ in BPn layer and $Pn(2)$ in FePn layer. Isostructural compound LaFeAsO has the similar structure of LaO layer with Ba$Pn(1)$ layer.

Ref. 19 that a magnetic ground state leads to very precise structural parameters. The calculated structural parameters are shown in Table I and compared to the experimental structural parameters of LaFeAsO.

There is a strong similarity between the $BaFeAs_2$ and $LaFeAsO_{1-x}F_x$ structure. The Fe-As bond length and angle in $BaFeAs_2$ are 2.404 Å and 112.54°, which are comparable to the values 2.412 Å and 113.55° in $LaFeAsO_{1-x}F_x$. However, there is a clear difference between BaAs layers and LaO layers in $LaFeAsO_{1-x}F_x$ although the structural group is the same. The Ba-As(1) bond length is much larger than the La-O bond length, such that As(1) atoms form a single layer separated from Ba atoms. This increases the FeAs interlayer distance, and the lattice constant along c direction becomes 35% larger than the value of $LaFeAsO_{1-x}F_x$. This indicates that $BaFeAs_2$ might have more two-dimensional properties than other Fe-based superconductors.

Substitution of As by Sb significantly modifies the structure. Fe-Sb bond length increases to 2.625 Å due to the large size of Sb ion, which substantially increases the lattice parameter a of $BaFeSb_2$. The Sb-Fe-Sb bond angle in $BaFeSb_2$ is 115.05° and is larger than the corresponding angle in $BaFeAs_2$. It has been suggested that the bond angle correlates with the transition temperature of Fe-based superconductors.[20] The highest T_c seems to be achieved in the structures with the tetrahedron angle closest to the ideal tetrahedron angle of 109.47°. This would suggest that doped $BaFeSb_2$ might have lower T_c than doped LaFeAsO and $BaFeAs_2$.

TABLE I. Calculated structural parameters of BaFePn_2 (Pn =As and Sb). The space group is $P4/nmm$ with the internal coordinates of Ba (0.25, 0.25, z_{Ba}), Fe (0.75, 0.25, 0.5), $Pn(1)$ (0.75, 0.25, 0.0), and $Pn(2)$ (0.25, 0.25, z_{Pn}). For comparison, the structural parameters of LaFeAsO is extracted from Ref. 1.

	$BaFeAs_2$	$BaFeSb_2$	LaFeAsO
a(Å)	3.999	4.430	4.035
c(Å)	11.826	11.977	8.741
z_{Ba}, z_{La}	0.2299	0.2395	0.142
z_{Pn}	0.6129	0.6177	0.651
Fe-$Pn(2)$ length (Å)	2.404	2.625	2.412
Ba-$Pn(1)$ length (Å)	3.384	3.624	2.367
$Pn(2)$-Fe-$Pn(2)$ angle (°)	112.54	115.05	113.55

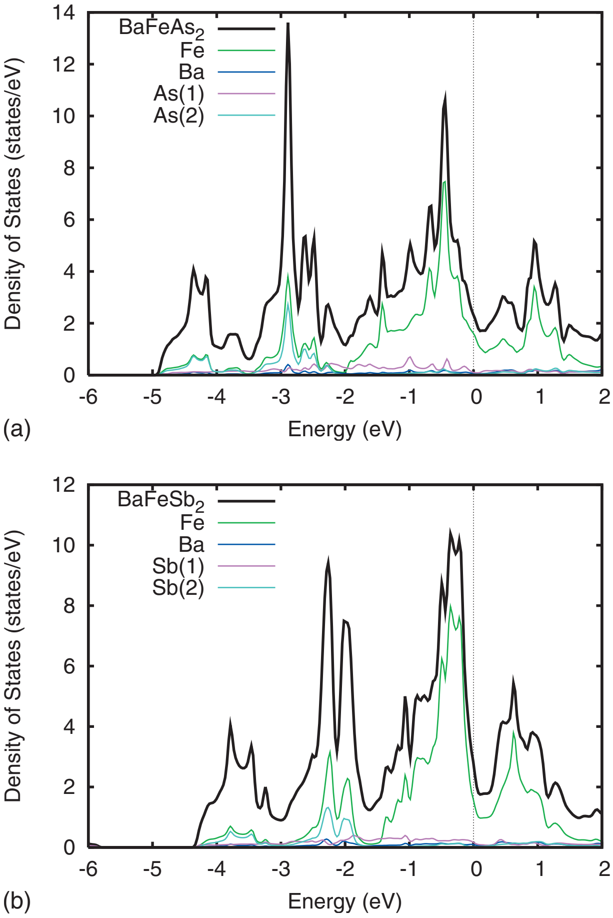

FIG. 2. (Color) Total and partial DOS of $BaFeAs_2$ and $BaFeSb_2$.

In order to check the electronic structure of BaFePn_2, we perform the calculation of density of states (DOS), band structures, and Fermi surfaces in paramagnetic phase with the structural parameters optimized in the magnetically ordered phase. Figure 2 shows total and partial DOS of $BaFeAs_2$ and $BaFeSb_2$. The general shape of Fe and As partial DOS in FeAs layer shows clear similarity between $BaFeAs_2$ and LaFeAsO. The DOS between −2 and 2 eV is dominated by Fe $3d$ states, and Sb $4p$ states are located around −3 eV, and their contribution at the Fermi level is negligible. At the Fermi level, the total DOS shows the same negative slope with the minimum slightly above the Fermi level, similar to the other FeAs superconductors within DFT.

The electronic structure of BaAs spacer layer shows a clear difference compared to LaO layer in LaFeAsO. The latter shows a clear insulating gap at the Fermi level, while the former is metallic. Due to the large density of Fe d states at E_F, the spacer layer however contributes a small percent-

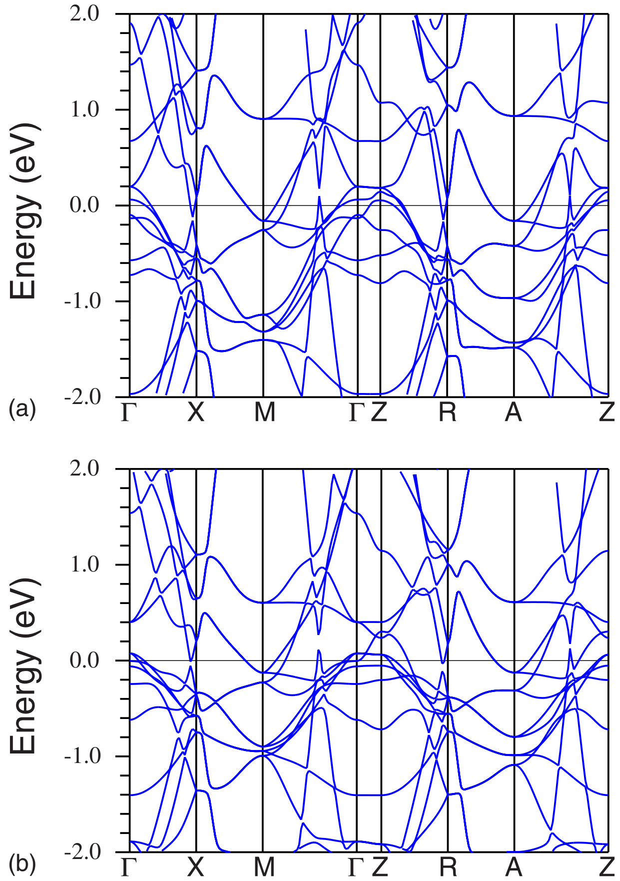

FIG. 3. (Color online) Band structure of $BaFeAs_2$ and $BaFeSb_2$.

age of states at E_F. Because of the large distance between the As(1) and the FeAs layer, the hybridization between As(1) and FeAs layer is negligible. In order to check the role of As(1) atoms, we calculated the electronic structure of BaFeAs in the absence of As(1) atoms with the same crystal structure of $BaFeAs_2$. The shape of partial Fe DOS does not change with the absence of As(1), which means that the As(1) atoms behave as separated single layer. Their role is hence to increase the spacing between the FeAs layers in z direction.

As expected from the structural parameters, the electronic structure of $BaFeSb_2$ is distinctly different from $BaFeAs_2$. Due to larger in-plane distance of Fe atoms, the width of Fe 3d partial DOS is substantially reduced and is confined between −1.5 and 1 eV. Hence the Fe moment in the magnetic state is expected to be large in $BaFeSb_2$ and the electronic correlations more important. Indeed the moment of Fe in the most stable magnetic state is $2.61\mu_B$ compared to $2.12\mu_B$ in $BaFeAs_2$. Hence the Fe d electrons are more localized in the structure with larger pnictide Pn.

The band structures of $BaFeAs_2$ and $BaFeSb_2$ are shown in Fig. 3. It shows many common features observed in other Fe-based superconductors. There are two hole pockets at Γ point and two electron pockets at M point. There is however a distinctive difference between the band structure of other known Fe superconductors and these two compounds studied here. There are a few very dispersive bands crossing the Fermi level, which are primarily coming from the As(1) atoms in the spacer layer. Near the Fermi level, these bands are however well decoupled from the bands coming from the FeAs layer.

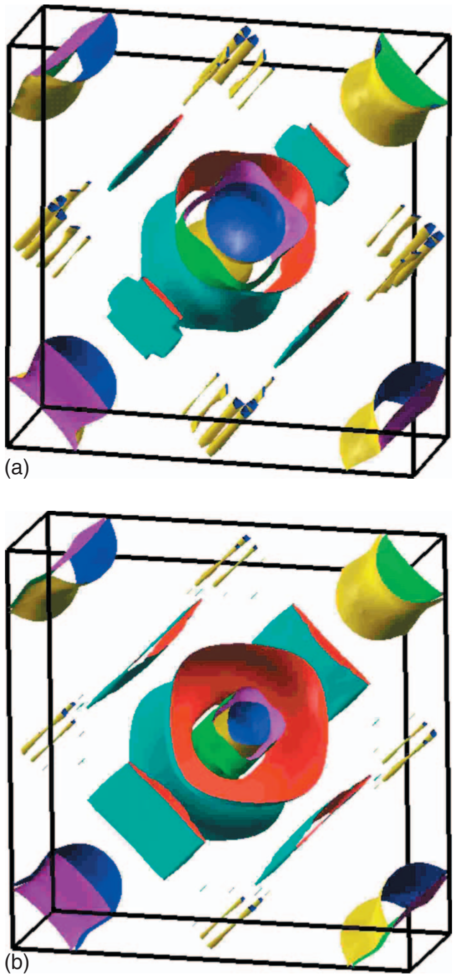

FIG. 4. (Color) Fermi surfaces of $BeFeAs_2$ and $BaFeSb_2$ in the first Brillouin zone centered at the Γ point.

Due to the similarity of band structure, the Fermi surface of $BaFeAs_2$ also shows clear similarity to that of Fe-based superconductors. Figure 4(a) shows the quasi-two-dimensional Fermi surfaces with cylindrical shape. There are two hole pockets at Γ points and two electron pockets at M point with the high degree of nesting between the hole and electron pockets. Due to the As(1) states at the Fermi level, there are additional Fermi surfaces with diamond shape connecting the X points. They clearly have a very two-dimensional character.

Although the mechanism for Fe-based superconductivity has not yet been established, a superconductivity appears in proximity to a magnetic phase. We checked the stability of the magnetic states in the two compounds. We found that stripe-type SDW phase is the most stable magnetic configuration among the commensurate magnetic states of a double unit cell. The stabilization energy of the SDW phase compared to the paramagnetic phase in $BaFeAs_2$ is $E_{SDW} = -161$ meV/Fe and in $BaFeSb_2$ is −434 meV/Fe. The magnetic moments in the muffin-tin radius of Fe atom is

$2.12\mu_B$ in the case of $BaFeAs_2$ and $2.61\mu_B$ in $BaFeSb_2$. The SDW magnetism is enhanced by the enhanced in-plane lattice constant.

The local density approximation and dynamical mean field theory (LDA+DMFT) calculations have demonstrated that, while the FeAs compounds are less correlated than the cuprates, they are not too far from the localization-delocalization transition.[7] As a result, it was found that at high temperatures LaFeAsO has a bad semimetal incoherent regime. We expect this regime to extend to higher dopings and pressures in the $BaFeSb_2$ compound, where the ratio of Hund's coupling and the crystal field splittings is larger than that in LaFeAsO or $BaFeAs_2$.

It is generally believed that two dimensionality is beneficial to superconductivity.[21] This compound, being more two dimensional than previously considered ones, if one uses the distance between the FeAs layers as a criteria, would then be a good candidate for high-temperature superconductivity. On the other hand, the superconducting temperature in 1111 compounds clearly decreases with decreasing c/a ratio, which would then suggest a lower T_c for the 112 family of compounds. Synthesis of the members of the 112 family would help elucidate further the role of two dimensionality in these compounds.

To summarize, we have suggested the synthesis of the 112 family of compounds, $BaFePn_2$, with Pn as a pnictide. Doping could be achieved by substitution of Ba by K or La. Using electronic structure tools, we have shown that these compounds have the same basic building block as that of the other known iron pnictide superconductors. We identified, however, a key difference in the character of the spacer block, which can provide hints as to the mechanism of superconductivity and the basic low-energy physics of these compounds.

The spin fluctuations of these compounds are very similar to the other iron-based superconductors, so we expect very similar variations in T_c with doping and pressure if a spin-fluctuation mechanism is operational. On the other hand, in a framework where the superconductivity is mediated by electronic polarizability,[12,13] the presence of additional metallic layers will strongly modify the superconducting transition temperature.

We predict that the magnetic moment is larger in the Sb member of the family which is *less* nested than its As relative. Experimental confirmation of this prediction would rule out weak-coupling approaches to this problem. Experimental determination of the T_c in these two compounds would clarify if nesting or the size of the magnetic moment is a better predictor of the superconducting transition temperature. Given the frantic pace of the research in this field we trust that the experimental answers to these important questions will be known in the very near future.

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